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Modeling mechanical properties of carbon molecular clusters and carbon nanostructural materials

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ABSTRACT

The concept of 2D elasticity of a graphene sheet together with the idea of stiffness of a single sp^3 bond have been applied to theoretical evaluating elastic properties of diverse carbon states. 2D elastic moduli have been extracted from data on elastic moduli of crystalline graphite. Stiffness of the sp^3 bond has been estimated from data on the elastic modulus of diamond. Efficiency of Van-der-Waals interaction has been taken from the elastic modulus C_{33} of crystalline graphite. Characteristics of single fullerene deformability have been computed by the molecular dynamics method. Theoretical estimations have been performed for single molecular clusters, pristine fullerite, HPHT phases of polymerized C_{60} , etc. The estimations are in good agreement with experimental data on elastic properties and nanoscale structure of carbon states. The approach is effective for establishing interrelation between nanostructure and elastic properties, for prediction and classification of nanostructure in novel carbon materials.

Three types of hybridized covalent bonds between of carbon atoms (sp^3 , sp^2 and sp) give rise a variety of macromolecular clusters and carbon nanostructural solids, which are essentially distinguished in their mechanical properties. Diversity of mechanical characteristics stems from the variability in nanostructural organization and from combination of different types of covalent bonds (sp^2 and sp^3) with Van-der-Waals interaction between molecular clusters. The purpose of the paper is to explain the elastic property diversity in the frame of simple mechanical models of different nanoscale structures using, in the main, data on elastic properties of well-known carbon states – graphite and diamond. Analysis of these models makes it possible to follow variations in elastic characteristic of carbon states in transition from one form of nanostructural organization to another.

The most of carbon states are formed by 2D structural units – plane or curved graphene sheets or closed molecular clusters (fullerenes, nanofilaments, etc) originated from these sheets. Van-der-Waals forces or covalent sp^3 bonds provide 3D linkage between the 2D graphite-like nanostructural elements. Diversity of carbon states actually results from two specific peculiarities of hybridized C-C bonds. The first is high lability – interatomic distances and valent angles are liable to vary over relatively wide range. Stressed sp^2 bonds cause bending graphene sheets – curved atomic sheets are inherent in many carbon states: carbon fibers, fullerenes, nanotubes and so on. The other feature of carbon is concurrent participation of different types of C-C bonds in formation of carbon states. Normally the spatial structure of carbon materials is formed by Van-der-Waals interaction between graphene sheets or molecular clusters. This interaction results in formation of soft and fragile materials (crystalline graphite and graphite materials, pristine fullerites, carbon nanotube paper). Under extreme conditions sp^3 bonds link molecular clusters

forming hard and ultrahard HPHT fullerene phases, neutron irradiated graphite, diamond-like films, etc.

Our mechanical models for evaluating elastic properties of solid carbon states include: (1) graphene sheets and 2D closed molecular clusters (fullerenes and nanofilaments) as elements of spatial construction, (2) Van-der-Waals interaction and (3) diamond-like sp^3 bonds as factors to assemble these structural elements into an integral construction. It allows discussing the mechanical properties in terms of 2D graphene sheet elasticity, stiffness of individual diamond-like bond and efficiency of Van-der-Waals force.

Carbon molecular clusters involve a significant number of atoms to treat them as macroscopic systems and to speak about their elastic properties. The surface elastic moduli \tilde{C}_{11} and \tilde{C}_{12} establish interrelation between the tensions τ_1 , τ_2 and strains ε_1 , ε_2 in the sheet plane:

$$\tau_1 = \tilde{C}_{11} \cdot \varepsilon_1 + \tilde{C}_{12} \cdot \varepsilon_2, \quad \tau_2 = \tilde{C}_{12} \cdot \varepsilon_1 + \tilde{C}_{11} \cdot \varepsilon_2 \quad (1)$$

Following to Ruoff's [1], the 2D elasticity of graphene sheets is evaluated from the in-plane elastic moduli C_{11} and C_{12} of crystalline graphite referred to a single sheet. The sheet density N in a graphite stack is derived from the interlayer distance d_0 . Using experimental data ($C_{11} = 1020 \text{ GPa}$, $C_{12} = 180 \text{ GPa}$ and $d_0 = 0.335 \text{ nm}$ [2]) we arrive at the surface moduli of a graphene sheet:

$$\tilde{C}_{11} = C_{11} \cdot d_0 = 341,7 \text{ Pa} \cdot \text{m}, \quad \tilde{C}_{12} = C_{12} \cdot d_0 = 60,3 \text{ Pa} \cdot \text{m} \quad (2)$$

The moduli \tilde{C}_{11} and \tilde{C}_{12} have been used in [1] to estimate the bulk elastic modulus $B_{C_{60}}$ of a single C_{60} molecule:

$$B_{C_{60}} = \frac{2}{3} (\tilde{C}_{11} + \tilde{C}_{12}) \cdot \frac{1}{R_{C_{60}}} = \frac{2}{3} (C_{11} + C_{12}) \cdot \frac{d_0}{R_{C_{60}}} \approx 800 \text{ GPa}, \quad (3)$$

$R_{C_{60}} = 0,35 \text{ nm}$ is the fullerene radius. The off-plane elastic characteristics (bending resistance) of the graphene sheet could not be estimated from properties of graphite. Response of an atomic layer to bending could not be considered as ordinary reaction of a macroscopic body: compression of the area below the neutral line and dilatation of the upper layers. To evaluate the response theoretical computation has been performed in the frame of molecular dynamics methods [3,4] for spherical configuration of a graphene sheet because of our special interest to elastic properties of superhard HPHT phases of C_{60} . The bending stiffness k of a graphene shell has been introduced to describe correlation between the point force f and the displacement $\Delta R_{C_{60}}$ of the shell induced this point load:

$$f = k \cdot \Delta R_{C_{60}} / R_{C_{60}}. \quad (4)$$

The calculated value of k is $57,6 \cdot 10^{-8} \text{ N}$.

Elasticity of a single sp^3 bond is characterized by stiffness K_{sp^3} of elementary tetrahedron associated with the bond with respect to the force f acting along the tetrahedron axis:

$$f \approx K_{sp^3} \cdot \varepsilon_h, \quad \varepsilon_h = \Delta h / h \quad (5)$$

The applied force induces the change Δh of the tetrahedron height h that we consider as the length of the intercluster link. Value of K_{sp} may be evaluated from magnitude of the elastic modulus $C_L^{<111>}$ of diamond along the $<111>$ direction. Diamond lattice is treated as an arrangement of parallel layers consisted of diamond tetrahedrons oriented along $<111>$ direction. Normal stress applied to the $\{111\}$ plane provides the force $f = \sigma \cdot S_0$ acting on an individual tetrahedron; $S_0 = \sqrt{3}/4 \cdot a^2$ is area of the $\{111\}$ plane associated with a single tetrahedron, a is length of *fcc* diamond lattice. The deformation ε_h of the elementary tetrahedron is equal to deformation induced by the applied stress in diamond

$$\varepsilon_h = \varepsilon^{<111>} = \sigma / C_L^{<111>}. \quad (6)$$

Starting from the value of $C_L^{<111>} = 1200$ GPa [5] the single sp^3 bond stiffness has been calculated:

$$K_{sp^3} = f / \varepsilon_h = C_L^{<111>} \cdot S_0 = \sqrt{3}/4 \cdot a^2 \cdot C_L^{<111>} = 6.58 \cdot 10^{-8} \text{ N}. \quad (7)$$

Efficiency of Van-der-Waals interaction is taken from the graphite elastic modulus C_{33} responsible for interlayer interaction between atomic sheets in crystalline graphite.

Elementary structural units described above are employed for the assessment of elastic properties in diverse carbon states. The attention is focused on evaluation of the bulk elastic modulus B (inverse compressibility). The bulk modulus is a natural elastic characteristic of a matter. The bulk modulus can be evaluated in the frame of the models for all feasible carbon states. Estimation of shear elastic characteristics requires more detailed description of interatomic interaction.

Let start the consideration from soft and fragile carbon states that are formed by plane or curved graphene sheets linked by Van-der-Waals forces. Crystalline and turbostratic graphite, pristine fullerite and nanotube materials represent this kind of the structural organization. Weak molecular forces between sheets, graphite clusters or fullerene molecules give the main contribution into elastic response of a matter. In crystalline graphite Van-der-Waals interaction hold together the stack of two-dimensional graphene sheets. Hydrostatic pressure p applied to a graphite sample above all else induces change of the distance between graphene sheets. So the bulk modulus B is close to the interlayer component C_{33} of the elastic matrix of graphite:

$$B_{gr} \approx C_{33} = 36 \text{ GPa}.$$

In turbostratic graphite and molecular crystals of pristine fullerite weak Van-der-Waals forces are responsible for interaction between graphite clusters or fullerene molecules in all directions uniformly. The bulk modulus B in these materials should be approximately 3 times smaller comparing with the value of B in crystalline graphite because hydrostatic pressure is able to change intercluster distances in three orthotropic directions. For a cubic molecular crystal of pristine fullerite the Hook equation gives values of strains ε_i ($i = 1, 2, 3$) induced by hydrostatic pressure p : $\varepsilon_i \approx p / C_{33}$; here the unidirectional elastic modulus of fullerite is approximated by the interlayer module C_{33} of graphite. The bulk deformation ε_V determines the value of the bulk modulus of crystalline C_{60} :

$$\varepsilon_V = \Delta V / V = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 = 3 \cdot p / C_{33}; \quad B_{pris} = C_{33} / 3 = 12 \text{ GPa}. \quad (8)$$

The theoretically estimated value of B is in good agreement with the experimentally obtained magnitude of 11 GPa. The little difference caused by curvature of fullerene molecules because the basis of our estimations is the molecular interaction between the plane graphene sheets.

The next group of carbon states includes substances in which covalent sp^3 partly replace the Van-der Waals interaction between molecular clusters. The substitution results in progressive stiffening carbon materials as increasing quantity of sp^3 covalent bonds. Mixture of sp^2 and sp^3 is characteristic for many graphite and diamond-like materials. But our consideration will be focused on high-pressure high-temperature (HPHT) phases of polymerized fullerite. Under HPHT conditions fullerites C_{60} and C_{70} undergo an intricate series of successive transformations caused by covalent sp^3 bonding of fullerene clusters. Mechanical properties of HPHT phases follow structural transformations. Polymerized fullerenes demonstrate a wide spectrum of phases with diverse nanostructure, elastic properties of that are available [6] to compare with our modeling estimations.

At first stages of polymerization fullerene balls are linked together into linear chains or planar structures [7] by pairs of sp^3 bonds (2+2 cycloaddition mechanism). Molecular chains and planes are held together by means of Van-der-Waals forces. Chains of polymerized C_{60} are aligned parallel into orthorhombic crystalline structure, planes provides tetrahedral or rhombohedral structure of 2D polymerized C_{60} . Van-der-Waals interaction between chains or planes of polymerized balls is much weaker than sp^2 and sp^3 bonds that form individual chains of fullerene molecules. Compressibility of the 1D or 2D polymerized states is determined by changing distances between chains and planes in directions perpendicular to the direction of alignment. Their bulk elastic moduli B should be close to the value specific for pristine crystalline fullerite or graphite ($10 \div 40$ GPa). The real values of B depend on topology of material structure. In pristine C_{60} Van-der-Waals interaction is responsible for all of three deformation ε_1 , ε_2 and ε_3 induced by hydrostatic pressure along the coordinate axes. Elastic response along each of the axes is described by the elastic coefficient C , which is close to the interlayer elastic parameter C_{33} of graphite: $C \approx C_{33}$. Because the bulk deformation ε_V involves all three values ε_1 , ε_2 and ε_3 :

$$\varepsilon_V = \varepsilon_1 + \varepsilon_2 + \varepsilon_3; \quad \varepsilon_1 \sim \varepsilon_2 \sim \varepsilon_3 \sim p / C,$$

we have arrived at the value $B_{prist} = C/3 \approx 12$ GPa in (8).

In 1D polymerized C_{60} hydrostatic pressure produces two strain ε_1 and ε_2 only, the third strain ε_3 along the direction of molecule alignment vanishes ($\varepsilon_3 \ll \varepsilon_{1,2}$). So the bulk elastic modulus B_{1D} of 1D polymerized C_{60} is by 1.5 time higher than the modulus of pristine C_{60} :

$$B_{1D} = p/(\varepsilon_1 + \varepsilon_2) = C/2 = (3/2) \cdot B_{prist} \approx 17 \text{ GPa} \quad (9)$$

In 2D polymerized state nanostructure is easily deformed only along one direction – perpendicular to the planes of covalently bounded fullerene molecules ($\varepsilon_{2,3} \ll \varepsilon_1$). The sp^3 covalent bonding makes 2D polymerized C_{60} 3 times stiffer comparing with pristine fullerene:

$$B_{2D} = p/\varepsilon_1 = C = 3 \cdot B_{prist} \approx 35 \text{ GPa} \quad (10)$$

Elastic modules of 1D and 2D polymerized C_{60} have been measured by the pulse time-resolved method of acoustic microscopy [6]. The experimental values of the bulk elastic modulus B for 1D and 2D polymerized C_{60} fullerites ($B_{1D} = 27$ GPa and $B_{2D} = 45$ GPa) are close to our estimations – 17 and 35 GPa respectively. Divergence of the experimental and calculated values

shows our calculations should be considered, as a qualitative way for estimating because real features of interaction between polymerized clusters has not been taken into account. Principally new situation arises when sp^3 covalent bonds pack up fullerene molecules into a 3D system. This type of C_{60} polymerization is realized at quite high pressure ($9 + 12$ GPa) and temperature (higher 1000°C). Elastic properties of 3D polymerized fullerenes have been measured by acoustic microscopy technique [6] and Brillouin scattering method; it was been shown the hardness and bulk modulus of some 3D polymerized phases are compared with these parameters of diamond. It necessary to underline 3D polymerized phases in practice are observed in crystalline (actually, polycrystalline) or partly disordered states. A few theoretical models of 3D crystalline structure of C_{60} fullerenes has been proposed [8,9].

For our estimations we employ the simplest model of a cubic 3D structure formed by fullerene molecules that are held together with double sp^3 covalent bonding (2+2 cycloaddition) in three perpendicular coordinate directions x_1, x_2, x_3 . The primary unit of this 3D structure is a fullerene molecule plus six perpendicular double sp^3 bonds. Elastic response of the structure to a stress applied along any of the coordinate axes is determined by the combined stiffness K of the series system of elastic elements involved a pair of covalent sp^3 bonds and bending resistance of the elastic sphere to a point force. Elastic characteristics of these elements have been described above. Using the bending stiffness k of a graphene shell and stiffness K_{sp^3} of a single sp^3 bond the expression for combined stiffness of the primary structural unit is written:

$$K = \frac{k \cdot (2K_{sp^3})}{\frac{l_1}{L} \cdot (2K_{sp^3}) + \frac{l_2}{L} \cdot k}, \quad (11)$$

l_1 – fullerene ball diameter ($\sim 7\text{\AA}$ [10]), l_2 – sp^3 tetrahedron height ($\sim 2\text{\AA}$), L – lattice parameter of 3D polymerized C_{60} ($\sim 8.5\text{\AA}$). According to our previous estimations: $k = 57.6 \cdot 10^{-8}\text{ N}$ and $K_{sp^3} = 6.6 \cdot 10^{-8}\text{ N}$. The resulting value of the combined stiffness $K = 31.3\text{ N}$ gives an elastic characteristics of the 3D polymer C_{60} structural unit. To pass to material properties we should transfer from the stiffness K to the elastic modulus C_{11} , characterizing one-dimensional elastic response of a matter dividing the stiffness K by area $S_{3D} = L^2$ of the lattice unit:

$$C_{11} = K/S_{3D} = 450\text{ GPa}. \quad (12)$$

Estimation of the bulk elastic modulus B_{3D} for the simple cubic 3D structure ($\epsilon_1 \sim \epsilon_2 \sim \epsilon_3 \sim p/C_{11}$) is:

$$B_{3D} = p/\epsilon_V = C_{11}/3 \approx 130\text{ GPa} \quad (13)$$

The value of B_{3D} has been calculated in approximation $C_{11} \gg C_{12}$. It gives the minimum of the value. Approximation $C_{11} = C_{12}$ leads to the maximum value of $B_{3D} \approx 400\text{ GPa}$. For the most solids $C_{11} \sim 2C_{12}$ and B_{3D} is about 260 GPa. Experimental values of bulk elastic modulus $B_{3D} \sim 160 \div 450\text{ GPa}$ [6] are in a good agreement with our calculations.

Experimental data point to existence of HPHT fullerene states with values of elastic moduli that are much bigger values calculated above. To explain these experimental results we propose a new model of structural organization and mechanical properties of HPHT phases. At very high pressure ($11 \div 13\text{ GPa}$) and temperature ($1200 \div 2000^\circ\text{C}$) fullerenes are linked through incorporation of sub-units of one cluster into cages of others (reaction of polycondensation [11]).

The cluster coalescence results in formation of rigid and tight-packed 3D graphene sheet network. We model the structure as a 3D system of mutually intersected graphene sheets packed parallel to x -, y -, z -directions and connected one to another by common atoms along lines of their intersections. The model seems to be a good approximation to estimate elastic response of ultrahard fullerite materials.

The elastic response of the model system is expressed through the surface elastic moduli \tilde{C}_{11} and \tilde{C}_{12} of a single graphene sheet and density $N = 1/b$ of graphene sheet package along each of the principal directions of packing (b – is a mean distance between neighbor atomic sheets along a given direction). Hydrostatic pressure p induces principal strains ε_1 , ε_2 and ε_3 along the principal axes. In each of three orthogonal directions the elastic response is caused by in-plane deformation of two orthogonal systems of intersecting sheets. For direction 1:

$$p = 2 \cdot \tilde{C}_{11} \cdot 1/b \cdot \varepsilon_1 + \tilde{C}_{12} \cdot 1/b \cdot (\varepsilon_1 + \varepsilon_3); \quad (13)$$

the same equations may be written for direction 2 and 3. This system of equations makes it possible to express the bulk deformation ε_V through the pressure p and to obtain the equation for the bulk elastic modulus B of the structure:

$$B = 2/3 \cdot (C_{11} + C_{12}) \cdot (d/b), \quad (14)$$

where C_{11} , C_{12} – in-plane elastic moduli of graphite; d and b – interlayer distances in graphite and in the model system accordingly. When the average size of the cluster units equals to the fullerene radius $R_0 = 0.355$ nm the expression (14) coincides with Rouff's calculations for the bulk elastic modulus of a free fullerene molecule: $B = 800$ GPa. The ultimate value of $B = 950$ GPa arises when the average interlayer distance b coincides with the one in graphite. Calculated values are able to explain extremely high values of the bulk elastic modulus of ultrahard fullerites $B = 550 \div 800$ GPa having been observed in experiments [6].

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